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THE EFFECTS OF THE THOMSON COEFFICIENT AND VARIABLE
RESISTIVITY ON THERMOELECTRIC HEAT PUMP PERFORMANCE

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RESISTIVITY ON THERMOELECTRIC HEAT PUMP PERFORMANCE

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NOMENCLATUREEnglish Letters

A	cross-sectional area of the thermoelement	cm ²
B	slope of the resistivity with respect to the absolute temperature	ohm-cm/ ^o K
E	dimensionless constant ($E = (\frac{\rho_a}{B} + T_h - T_a)(\frac{1}{T_h - T_c})$)	
I	electrical current	amps
k	thermal conductivity	watts/cm- ^o K
L	length of thermoelement	cm
Q	rate of heat removal	watts
R	electrical resistance	ohms
S	Seebeck coefficient	volts/ ^o K
t	time	seconds
T	absolute temperature	^o K
u	dimensionless position variable ($u = \frac{x}{L}$)	
U	electrical and thermal energy entering or leaving the thermoelement	joules
V	voltage	volts
x	position variable	cm
Y	dimensionless variable ($Y = \frac{I \tau L}{k A}$)	

Greek Letters

θ	dimensionless temperature variable ($\theta = \frac{T}{T_h - T_c}$)	
ρ	electrical resistivity	ohm-cm
τ	Thomson coefficient	volts/ ^o K

SUMMARY

Steady-state, closed form solutions are presented for the temperature distribution, heat removal, and coefficient of performance of an insulated, thermoelectric heat pump. The solutions are derived from the differential equation for the temperature distribution within a thermoelement. The Seebeck coefficient is expressed as a logarithmic function of temperature. This expression permits the performance of elements made of thermoelectric materials with the same average Seebeck coefficient but with different values of the Thomson coefficient to be compared. An expression for electrical resistivity as a linear function of temperature is also introduced. Thus, the performance of heat pump elements made of materials having the same average resistivity but having resistivities that are different linear functions of temperature can be compared.

A specific numerical example is studied in order to evaluate the effect of the Thomson coefficient and variable resistivity on the heat removal and coefficient of performance. Values of the Thomson coefficient ranging from 0 to $\pm 200 \times 10^{-6}$ volts per degree Kelvin and values for resistivity with linear slopes varying from 0 to 6×10^{-6} ohm-cm per degree Kelvin are used. With the aid of the Burroughs 220 computer, the equations are solved for the maximum heat removal and the maximum coefficient of performance corresponding to each assumed value of Thomson coefficient and resistivity slope. Analytical results for the effect of the Thomson coefficient and variable resistivity on the maximum temperature difference of a thermoelement are also presented.

The results based upon the numerical example show that materials having positive Thomson coefficients can increase the element heat removal by 35 per cent over a material with zero Thomson coefficient. Similarly, when using materials with positive Thomson coefficients, the coefficient of performance is as much as 18 per cent greater than with a material with zero Thomson coefficient. A numerical example is given which shows that a positive Thomson coefficient can improve the maximum temperature difference by several degrees Kelvin. The same example shows almost negligible change in maximum temperature difference as the resistivity slope varies. Heat removal decreases by no more than 5 per cent when the material resistivity increases linearly with temperature. The coefficient of performance, however, improves by up to 8 per cent as the slope of the resistivity increases.

On the basis of this study, it is concluded that the Thomson coefficient and variable resistivity can have considerable effect on heat pump performance. Therefore, these two parameters should always be included in any theoretical analysis of heat pump performance. The use of an average parameter approach is shown to produce considerable error. Because of the substantial increase in performance that may be attained using elements with positive Thomson coefficients, thermoelectric materials with the highest, positive Thomson coefficients should normally be selected for heat pump applications if the material properties are otherwise similar. It should also be possible to achieve some improvement in element performance by properly selecting materials with regard to the variation of their resistivity with temperature.

CHAPTER I

INTRODUCTION

Previous Development of Heat Pump Performance Equations

With the development of improved thermoelectric materials, the thermoelectric heat pump has become a practical method of refrigeration for certain applications. Two such applications are a small, portable refrigerator recently put on the market for home use, and a thermoelectric refrigeration unit being considered by the Navy for submarine application.

Several workers in this field have investigated mathematical models of the temperature distribution within a thermoelectric element. From the models, they have developed equations for performance factors such as: (1) the heat pumped, (2) the coefficient of performance, and (3) the no-load temperature difference in a thermoelectric heat pump. These factors are defined briefly here, but are discussed more fully in Chapter III. The heat pumped or heat removal, Q_c ,* is the amount of heat that is removed from the cold junction of the thermoelectric element per unit time. The coefficient of performance, C.O.P., is the ratio of the heat pumped to the total electrical power input to the thermoelement. The final performance factor, the no-load temperature difference, is the temperature difference that can be attained between the two ends of the thermoelement when the cold junction is thermally insulated.

* Mathematical symbols are defined in the Nomenclature which appears on page vii.

The investigators usually made certain simplifying assumptions in order to obtain the necessary equations. A cylindrical insulated element has often been selected as the basic model for the development of equations for heat pump performance. Accompanying assumptions for the equations generally included: (1) constant resistivity, (2) constant thermal conductivity, and (3) constant Seebeck coefficient.* Only limited work has been carried out to indicate how performance criteria are affected if properties of the thermoelement are not considered constant, but are allowed to vary with temperature.

In this study, equations for heat pump performance are developed assuming resistivity varies linearly with temperature and the Thomson coefficient is constant. Specific values for the properties of the thermoelement are substituted into the equations in order to determine how and to what extent the performance is affected by linearly varying resistivity and by the influence of the Thomson coefficient.

Review of Earlier Analytical Studies in Thermoelectrics

One of the earlier studies in the field of thermoelectric elements was carried out by A. F. Ioffe (10). His simplified analysis assumed that the thermal conductivity, resistivity, and Seebeck coefficient were independent of temperature. Because the Seebeck coefficient was not assumed to vary with temperature, the Thomson coefficient was zero. The analysis, therefore, provided no insight into the effects of the Thomson coefficient or variable resistivity on heat pump performance. Another analysis completed by Ioffe (10) assumed a constant value for the Thomson

* From the Kelvin relations (7), a constant Seebeck coefficient results in a zero Thomson coefficient.

coefficient, resistivity, and thermal conductivity. An approximate substitution was made for the Thomson coefficient in terms of the Seebeck coefficient and temperature to obtain expressions for heat removal and coefficient of performance. However, no attempt was made by Ioffe to numerically evaluate the effect of the Thomson coefficient on thermoelement performance. In addition, only an average value of resistivity was used in the analysis.

Norwood (14) investigated the effects of temperature-dependent properties on the performance of a thermoelectric heat pump. He assumed that the thermal conductivity was variable and, therefore, was forced to use numerical integration in order to obtain the no-load temperature difference. The no-load temperature difference was the only performance factor analyzed. However, his results are applicable in part to this study and will be presented in greater detail later on.

Siegla and Chaddock (18) presented curves to evaluate the validity of using constant value properties to determine the temperature distribution with a thermoelectric heat pump. Curves of the temperature distribution were shown for: (1) the "exact" solution, (2) a solution using the cold junction values of k and ρ , (3) a solution using the hot junction values of k and ρ , and (5) an "exact" solution neglecting the Thomson coefficient. Their "exact" solution was based upon the assumptions of linearly varying resistivity, constant Thomson coefficient, and a value of k calculated from the average of the hot and cold junction values. These assumptions were based upon results given by Norwood (14). The investigators claimed that by using these relationships, the solution "should be very near to an exact one-dimensional solution." They

concluded that a constant property analysis that evaluates the material properties at the length-average temperature provides close agreement with an "exact" analysis if the Thomson effect is a minor one. However, they did not attempt to evaluate the extent of the influence of the Thomson effect or variable resistivity on heat pump performance.

Sunderland and Burak (20) obtained analytical expressions for the power and efficiency of a thermoelectric generator assuming the Thomson coefficient, thermal conductivity, and resistivity were all constant. They used specific values for the thermoelement properties in a numerical example to show the effect of the Thomson coefficient on power and efficiency. The average value of the Seebeck coefficient for the thermoelectric material was held constant while the Thomson coefficient was allowed to take on several values. The effect of the Thomson coefficient on the performance of a thermoelectric heat pump was not considered.

Ybarrondo and Sunderland (21) evaluated the effect of surface heat transfer and finite fins on the thermoelectric heat pump performance. They developed equations for the optimum heat removal, no-load temperature difference, and coefficient of performance with respect to the current for a partially insulated thermoelement having finite fins. The analysis showed that performance can be improved with surface heat transfer. Curves were also presented showing the effect of fin size on element performance. However, the investigators assumed that resistivity was constant and that the Thomson coefficient was zero.

Ybarrondo and Sunderland (22) also investigated the influence of spatially dependent properties on the performance of a thermoelectric

heat pump. The Seebeck coefficient, electrical resistivity, and thermal conductivity were assumed to vary linearly with position along the thermoelement. Equations are presented for heat removal, no-load temperature difference, and coefficient of performance using spatially dependent properties. A numerical technique was used to maximize the heat-removal, no-load temperature difference, and coefficient of performance with respect to the current. The results showed that the maximum heat removal, C.O.P., and no-load temperature difference were improved when electrical resistivity and Seebeck coefficient had small linear variations with position. The effect of thermal conductivity was found to be small as compared to the other two properties. In this analysis the authors did not attempt to evaluate the effect on heat pump performance when resistivity varies linearly with temperature rather than with position. Nor did they examine the effect of the Thomson coefficient on heat pump performance.

Sherman, Heikes, and Ure (9) presented a method of numerical integration by which numerical values for the coefficient of performance and the heat pumped were obtained for a thermoelectric heat pump. Similarly, values for the efficiency of a thermoelectric generator were obtained. This method took into account the temperature dependence of the resistivity, Seebeck coefficient, and figure of merit.

They assigned theoretical temperature dependent properties to obtain four numerical examples. For each example the numerical solutions for the C.O.P. and the heat pumped--based on temperature dependent properties--were compared with solutions obtained by using average values for the properties. A similar procedure was carried out for the

efficiency of a generator.

By allowing the resistivity, Seebeck coefficient, and figure of merit to be different functions of temperature for each of the four examples, the authors were able to make some general conclusions about thermoelement performance. They noted that "for the case of k and τ independent of temperature and ρ linear with temperature, the temperature dependence of the resistivity affects the fraction of both the Joule and Thomson heats going to the cold junction." To improve C.O.P., they also found it desirable to have a Thomson coefficient that has the effect of removing heat from the cold junction. For the thermoelectric element considered, a positive Thomson coefficient tended to remove heat from the cold junction whereas a negative Thomson coefficient had the effect of adding heat. At the given operating conditions, the maximum C.O.P. was 0.183 with a positive Thomson coefficient and 0.148 for a negative Thomson coefficient.

Because the paper considered only four specific examples, no general conclusions could be drawn concerning the effect of the Thomson coefficient and variable resistivity on either heat pump or generator performance.

Burshtein (3) derived equations for the steady-state flow of heat through a thermoelectric element. He included, among other equations, an expression for steady-state flow of heat assuming resistivity to be a linear function of temperature and Thomson coefficient to be a constant. However, he did not attempt to develop equations for the performance of the thermoelement using these assumptions; nor did he

investigate numerically what effect linear resistivity or the Thomson coefficient had on the flow of heat.

In summary, researchers in thermoelectrics have often assumed the resistivity to be constant and the Thomson coefficient to be zero. The review given of the past literature indicates that some analyses did assume that the resistivity was variable and also did take the Thomson coefficient into account. These papers, however, did not attempt to evaluate how changes in those two parameters might affect the performance of a thermoelectric heat pump. This thesis investigates the effect of the Thomson coefficient and variable resistivity on heat pump performance.

CHAPTER II

MATHEMATICAL MODEL

Differential Equation for Temperature Distribution

The thermoelectric heat pump used for analysis is shown in Figure 1. The element is assumed to be connected to a voltage source so that a D.C. current will flow in the direction indicated. It is perfectly insulated over its entire length from $x = 0$ to $x = L$. Although a paper by Rollinger and Sunderland (17) affirms that better performance may be achieved if the element is only partially insulated, this case will not be considered here. The hot and cold junctions are to be maintained at fixed temperatures of T_h and T_c , respectively, and the cross-sectional area A is constant.

The differential equation for the one-dimensional steady-state temperature distribution in the thermoelement is derived in Appendix A. The resulting analysis gives

$$\frac{d}{dx} \left(k(T)A \frac{dT}{dx} \right) - I\tau(T) \frac{dT}{dx} + \frac{I^2 \rho(T)}{A} = 0 \quad (2-1)$$

where k is the thermal conductivity, I the electrical current, ρ the electrical resistivity and τ the Thomson coefficient. If the thermal conductivity k and the Thomson coefficient τ are assumed to be constant, and if the resistivity is given by $\rho = \rho_a + B(T - T_a)$, then Equation (2-1) can be written as

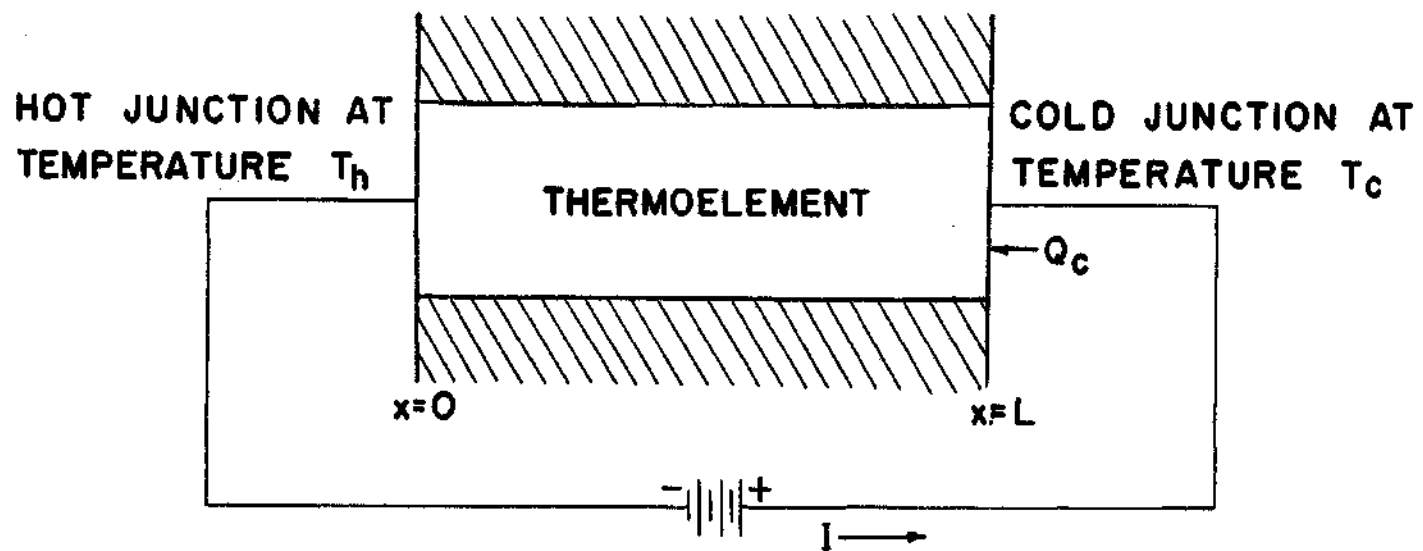


Figure 1. Thermoelectric Element Used as a Heat Pump.

$$\frac{d^2T}{dx^2} - \frac{I_T}{kA} \frac{dT}{dx} + \frac{I^2BT}{kA^2} + \frac{I^2(\rho_a - BT_a)}{kA^2} = 0 \quad (2-2)$$

The justification for assuming that the conductivity is constant is given in a paper by Parrott (15). He found that when k was assumed constant, the maximum error made in calculating the temperature distribution was less than 1 per cent. This analysis applied to refrigerating elements operating below 50°C.

Variable Resistivity

Over the temperature range generally used for refrigerating elements, the resistivity can be closely approximated as a linear function of the absolute temperature. Therefore, the resistivity was assumed to be

$$\rho = \rho_a + B(T - T_a) \quad (2-3)$$

where ρ_a is the average resistivity for the hot and cold junction, $\rho_a = (\rho_c + \rho_h)/2$, and T_a is the temperature at which $\rho = \rho_a$. Since the resistivity varies linearly with temperature, T_a will equal $(T_h + T_c)/2$. The symbol B is the rate of change of the resistivity with respect to the absolute temperature and is a positive constant for the element under consideration. It is assumed positive because the rate of change of the resistivity with respect to temperature is positive for semiconductor materials used for refrigeration. By representing the resistivity in this manner, elements made of materials having the same

average resistivity but different values of B may be compared. In Figure 2, the resistivity is plotted as a function of temperature for bismuth telluride (14). Using Equation (2-3), resistivity is also plotted for various values of B when $\rho_a = 0.001$ ohm-cm and $T_a = 275^\circ\text{K}$.

Constant Thomson Coefficient

From the assumption of constant Thomson coefficient, the Seebeck coefficient becomes a logarithmic function of temperature. By the Kelvin relations (7), the Thomson coefficient and Seebeck coefficient are related as follows

$$\tau = T \frac{dS}{dT} \quad (2-4)$$

Since τ is constant, Equation (2-4) can be integrated between the limits S and S_b and T and T_b to yield

$$S = S_b + \tau \ln \frac{T}{T_b} \quad (2-5)$$

The constant S_b is the average value of the Seebeck coefficient for the hot and cold junctions, $S_b = (S_h + S_c)/2$, and T_b is the temperature for which $S = S_b$. By allowing S_b to be the average value of the Seebeck coefficient between T_c and T_h , elements made of thermoelectric materials with different Thomson coefficients but the same average Seebeck coefficient can be compared. Figure 3 shows a plot of Seebeck coefficient versus temperature for bismuth telluride as taken from experimental results by Norwood (14). The plot shows that S_b will equal $(S_h + S_c)/2$

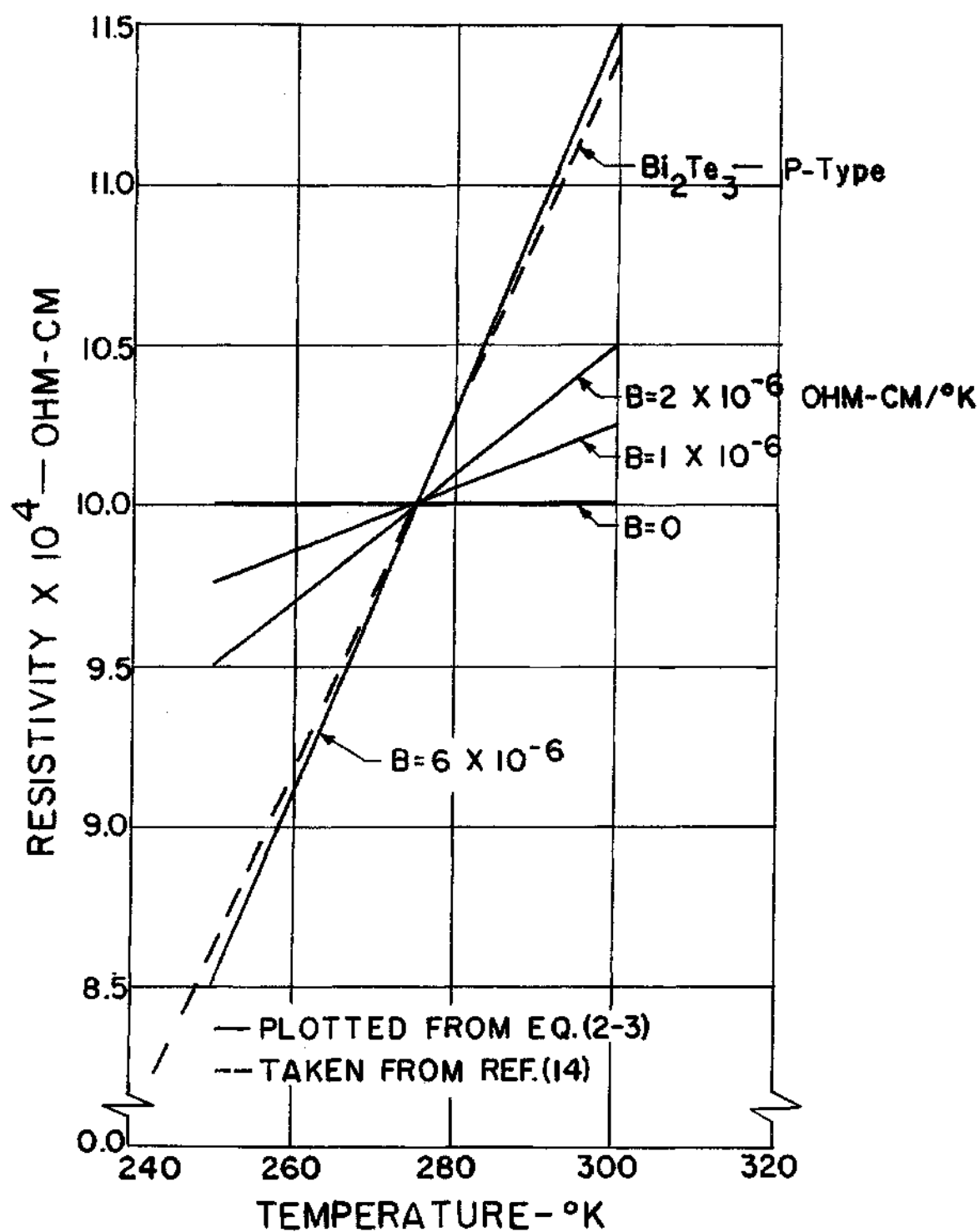


Figure 2. Resistivity as a Function of Temperature for Several Heat Pump Elements.

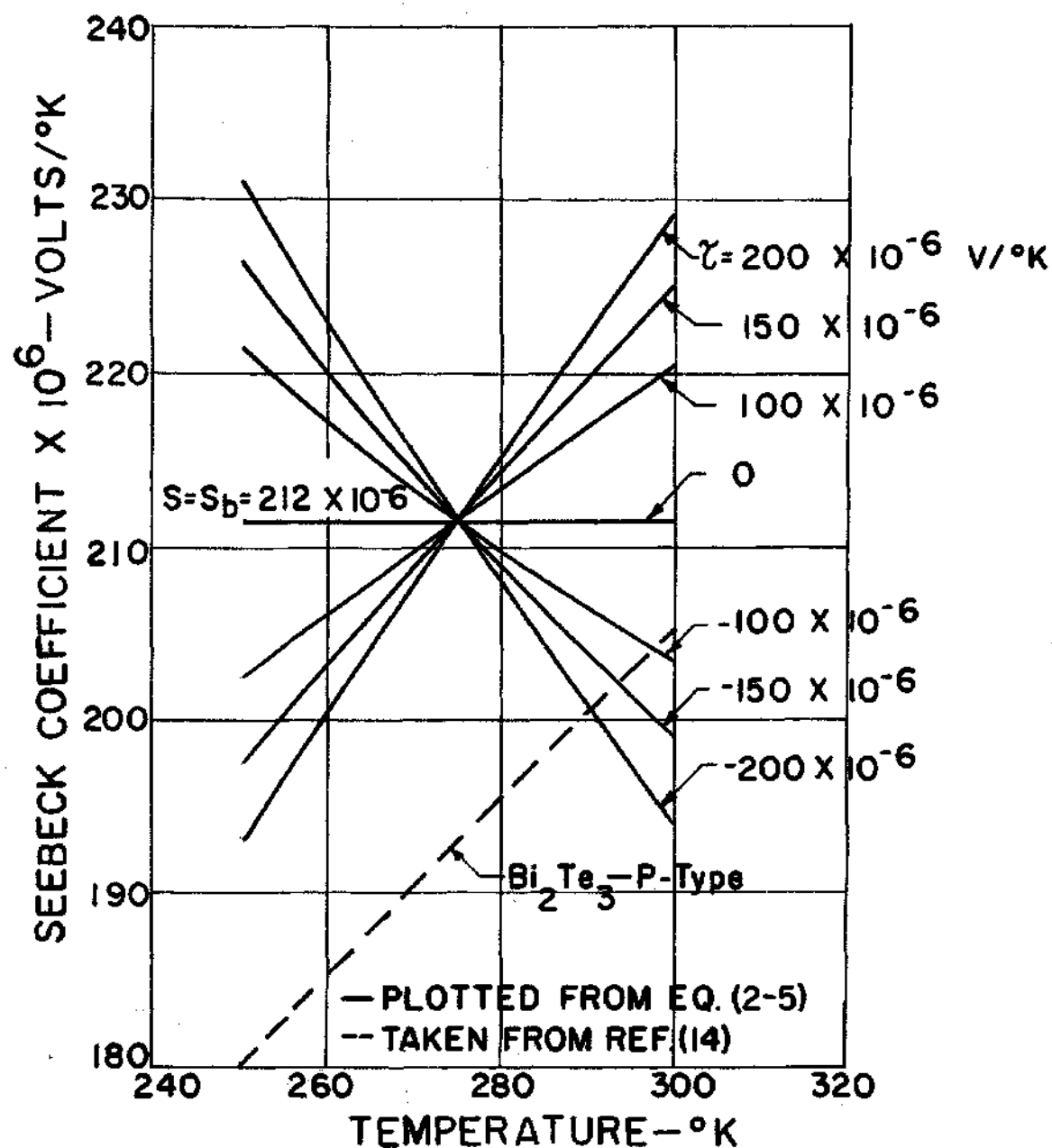


Figure 3. Seebeck Coefficient as a Function of Temperature for Several Heat Pump Elements.

at approximately 275°K. Using Equation (2-5), positive and negative values of τ are also plotted when $S_D = 212 \times 10^{-6}$ volts/°K and $T_D = 275^\circ\text{K}$. The value of 212×10^{-6} volts/°K is given in Reference 21 as being typical for present heat pump materials.

Equation (2-2) now remains to be solved for the temperature distribution when B is positive and τ is positive or negative. These solutions will be used to derive equations for the heat pumped and the coefficient of performance. Various values for τ and B will then be substituted into the equations to obtain the maximum coefficient of performance and the maximum heat pumped for the element.

CHAPTER III

PERFORMANCE OF AN INSULATED THERMOELEMENT

WITH CONSTANT THOMSON COEFFICIENT AND VARIABLE RESISTIVITY

Solution of the Temperature Distribution Equation

As given previously, the differential equation for the temperature distribution in an element of a heat pump is

$$\frac{d^2T}{dx^2} - \frac{IT}{kA} \frac{dT}{dx} + \frac{I^2 BT}{kA^2} + \frac{I^2(\rho_a - BT_a)}{kA^2} = 0 \quad (2-2)$$

The boundary conditions for Equation (2-2) are

$$T(0) = T_h \quad (3-1)$$

$$T(L) = T_c \quad (3-2)$$

where T_h and T_c are the temperatures of the hot and cold junctions, respectively.

For convenience, Equation (2-2) can be written in another form. Let u , the dimensionless position along the element, be defined by

$$u = \frac{x}{L} \quad (3-3)$$

The temperature can be expressed in dimensionless form as

$$\theta(u) = \frac{T(x)}{T_h - T_c} \quad (3-4)$$

By setting

$$Y = \frac{I\tau L}{kA} \quad (3-5)$$

the equation is transformed to

$$\frac{d^2\theta}{du^2} - Y \frac{d\theta}{du} + \frac{kBY^2\theta}{\tau^2} + \frac{kY^2(\rho_a - BT_a)}{\tau^2(T_h - T_c)} = 0 \quad (3-6)$$

The boundary conditions become

$$\theta(0) = \theta_h \quad (3-7)$$

$$\theta(1) = \theta_c \quad (3-8)$$

Equation (3-6) is a second order linear differential equation of the form

$$c_1 \frac{d^2\theta}{du^2} + c_2 \frac{d\theta}{du} + c_3\theta = c_4 \quad (3-9)$$

where c_1 , c_2 , c_3 , and c_4 are constants. Its solutions are well-known

for all values of the constants. Therefore, the temperature distribution can be obtained for all values of τ and B . There are six possible solutions to the equation, depending on the relative magnitudes of τ^2 , $4Bk$, and B . If $\tau^2 > 4Bk$ and $|B| > 0$, then

$$\theta(u) = \exp(Yu/2) \left[E \cosh(Yu\sqrt{\tau^2 - 4Bk}/2\tau) + \frac{E-1-E \exp(Y/2) \cosh(Y\sqrt{\tau^2 - 4Bk}/2\tau)}{\exp(Y/2) \sinh(Y\sqrt{\tau^2 - 4Bk}/2\tau)} \times \sinh(Yu\sqrt{\tau^2 - 4Bk}/2\tau) \right] - \frac{\rho_a}{B(T_h - T_c)} + \theta_a \quad (3-10)$$

where

$$E = \frac{\rho_a}{B(T_h - T_c)} + \theta_h - \theta_a \quad (3-11)$$

For $\tau^2 = 4Bk$ and $|B| > 0$,

$$\theta(u) = \exp(Yu/2) \left[E + \frac{[E-1-E \exp(Y/2)] u}{\exp(Y/2)} \right] - \frac{\rho_a}{B(T_h - T_c)} + \theta_a \quad (3-12)$$

If $4Bk > \tau^2$ and $B > 0$, then

$$\theta(u) = \exp(Yu/2) \left[E \cos(Yu\sqrt{4Bk - \tau^2}/2\tau) + \frac{E-1-E \exp(Y/2) \cos(Y\sqrt{4Bk - \tau^2}/2\tau)}{\exp(Y/2) \sin(Y\sqrt{4Bk - \tau^2}/2\tau)} \times \sin(Yu\sqrt{4Bk - \tau^2}/2\tau) \right] - \frac{\rho_a}{B(T_h - T_c)} + \theta_a \quad (3-13)$$

$$\frac{\rho_a}{B(T_h - T_c)} + \theta_a$$

For the condition where $B = 0$, Equation (3-6) reduces to

$$\frac{d^2\theta}{du^2} - Y \frac{d\theta}{du} + \frac{kY^2\rho_a}{\tau^2(T_h - T_c)} = 0 \quad (3-14)$$

The solution for Equation (3-14) subject to the boundary conditions given in Equations (3-7) and (3-8) is

$$\theta(u) = \exp(Yu) \left\{ \frac{\frac{kY}{(T_h - T_c)\tau^2} + 1}{1 - \exp(Y)} \right\} + \frac{kY\rho_a u}{(T_h - T_c)\tau^2} + \quad (3-15)$$

$$\theta_h = \left\{ \frac{\frac{kY}{(T_h - T_c)\tau^2} + 1}{1 - \exp(Y)} \right\}$$

If $\tau = 0$ and $B > 0$, Equation (2-2) reduces to

$$\frac{d^2\theta}{du^2} + \frac{I^2 L^2 B \theta}{kA^2} + \frac{I^2 L^2}{kA^2} (\rho_a - BT_a) = 0 \quad (3-16)$$

When applying boundary conditions (3-7) and (3-8), the solution to Equation (3-16) is

$$\theta(u) = \frac{E-1-E \cos(IL\sqrt{Bk}/kA)}{\sin(IL\sqrt{Bk}/kA)} \times \sin(ILu\sqrt{Bk}/kA) + \quad (3-17)$$

$$E \cos(ILu\sqrt{Bk}/kA) - \frac{\rho_a}{B(T_h - T_c)} + \theta_a$$

Although this analysis considers only positive values of B, the solution for $\tau = 0$ and $B < 0$ could be obtained by applying Equation (3-10).

For $\tau = 0$ and $B = 0$, Equation (2-2) becomes

$$\frac{d^2\theta}{du^2} + \frac{I^2\rho_a L^2}{kA^2(T_h - T_c)} = 0 \quad (3-18)$$

The solution for Equation (3-18) using the conditions given by boundary Equations (3-7) and (3-8) is

$$\theta(u) = -\frac{I^2\rho_a L^2 u^2}{2kA^2(T_h - T_c)} + \left[\frac{I^2\rho_a L^2}{2kA^2(T_h - T_c)} - 1 \right] u + \theta_h \quad (3-19)$$

Equations (3-10), (3-12), (3-13), (3-15), (3-17), and (3-19) comprise the six solutions for the temperature distribution in a thermoelement.

The Performance Equations

The performance of a thermoelectric heat pump is judged on the

basis of: (1) the heat Q_c that can be removed from the cold junction, (2) the coefficient of performance that can be achieved, and (3) the maximum temperature difference across the element when the cold junction is thermally insulated.

Heat Removal

The heat removed from the cold junction may be expressed by

$$Q_c = kA \left. \frac{dT}{dx} \right|_{x=L} + S_c IT_c \quad (3-20)$$

where S_c is the Seebeck coefficient at the cold junction. The first term on the right side of Equation (3-20) is the heat conducted to the cold junction. The second term is the heat removed due to the Peltier effect at the junction. From Equation (2-5), the Seebeck coefficient, S_c , may be expressed as

$$S_c = S_b + \tau \ln \frac{\theta_c}{\theta_b} \quad (3-21)$$

Equation (3-20) can then be written as

$$Q_c = \frac{kA(T_h - T_c)}{L} \left. \frac{d\theta}{du} \right|_{u=1} + (S_b + \tau \ln \frac{\theta_c}{\theta_b}) \frac{YkAT_c}{L\tau} \quad (3-22)$$

Again, there are six possible solutions for Q_c . From Equations (3-22) and (3-10)

$$Q_c = \frac{kA(T_h - T_c) Y}{2L} \left\{ E - 1 + \frac{\sqrt{\tau^2 - 4Bk} (E - 1)}{\tau \tanh(Y\sqrt{\tau^2 - 4Bk} / 2\tau)} - \right. \quad (3-23)$$

$$\left. \frac{E \exp(Y/2) \sqrt{\tau^2 - 4Bk}}{\sinh(Y\sqrt{\tau^2 - 4Bk} / 2\tau)} + 2(S_b + \tau \ln \frac{\theta_c}{\theta_b}) \frac{\theta_c}{\tau} \right\}$$

for $\tau^2 > 4Bk$ and $|B| > 0$.

For $\tau^2 = 4Bk$ and $B > 0$

$$Q_c = \frac{kA(T_h - T_c)}{L} \left[(E - 1) (Y/2 + 1) - \right. \quad (3-24)$$

$$\left. E \exp(Y/2) + (S_b + \tau \ln \frac{\theta_c}{\theta_b}) \frac{Y\theta_c}{\tau} \right]$$

when combining Equations (3-22) and (3-12).

From Equations (3-22) and (3-13)

$$Q_c = \frac{kA(T_h - T_c) Y}{2L} \left[E - 1 + \frac{(E - 1) \sqrt{4Bk - \tau^2}}{\tau \tan(Y\sqrt{4Bk - \tau^2} / 2\tau)} + \right. \quad (3-25)$$

$$\left. \frac{E \exp(Y/2) \sqrt{4Bk - \tau^2}}{\tau \sin(Y\sqrt{4Bk - \tau^2} / 2\tau)} + 2(S_b + \tau \ln \frac{\theta_c}{\theta_b}) \frac{\theta_c}{\tau} \right]$$

for $4Bk > \tau^2$ and $B > 0$.

For the case where $B = 0$, Equations (3-22) and (3-15) yield

$$Q_c = \frac{kA(T_h - T_c) Y}{L} \left[\frac{\exp(Y)}{1 - \exp(Y)} \left(\frac{Y \rho_a k}{\tau^2(T_h - T_c)} + 1 \right) + \right. \quad (3-26)$$

$$\left. \frac{\rho_a k}{\tau^2(T_h - T_c)} + (S_b + \tau \ln \frac{\theta_c}{\theta_b}) \frac{\theta_c}{\tau} \right]$$

For $\tau = 0$ and $B > 0$, Equations (3-22) and (3-17) give

$$Q_c = I(T_h - T_c) \left[\sqrt{Bk} \left(\frac{(E-1) \cos(IL\sqrt{Bk}/kA) - E}{\sin(IL\sqrt{Bk}/kA)} \right) + S_b \theta_c \right] \quad (3-27)$$

When $B = 0$ and $\tau = 0$,

$$Q_c = - \frac{I^2 \rho_a L}{2A} - \frac{kA(T_h - T_c)}{L} + S_b IT_c \quad (3-28)$$

from Equations (3-22) and (3-19). Equation (3-28) is the equation for heat removal given by Ioffe (10).

Coefficient of Performance

The coefficient of performance is the ratio of the heat removed from the cold junction to the total electrical power input to the element. Thus,

$$\text{C.O.P.} = \frac{Q_c}{\frac{I^2}{A} \int_{x=0}^{x=L} \rho \, dx + I \int_{T_c}^{T_h} S dT} \quad (3-29)$$

or after substitutions

$$\text{C.O.P.} = Q_c / \left\{ \frac{Y^2 k^2 A}{L \tau^2} \int_{u=0}^{u=1} \left[(\rho_a - B T_a) + B(T_h - T_c) \theta \right] du \right. \\ \left. + \frac{YkA}{L} (T_h - T_c) \int_{\theta_c}^{\theta_h} S d\theta \right\} \quad (3-30)$$

The first term in the denominator of Equation (3-30) is the power expended by Joule heating. The second term is the power necessary to offset the Seebeck voltage created by the temperature difference across the element. By making use of Equation (2-5), the second integral may be written as:

$$\int_{\theta_c}^{\theta_h} S d\theta = S_D + \tau \left[\theta_h \left(\ln \frac{\theta_h}{\theta_a} - 1 \right) - \theta_c \left(\ln \frac{\theta_c}{\theta_a} - 1 \right) \right] \quad (3-31)$$

The coefficient of performance has six solutions. By using Equations (3-23), (3-30), and (3-10),

$$\text{C.O.P.} = \left\{ \tau(E - 1) + \frac{(E - 1) \sqrt{\tau^2 - 4Bk}}{\tanh(Y \sqrt{\tau^2 - 4Bk} / 2\tau)} - \right. \quad (3-32)$$

$$\begin{aligned}
& \frac{E \exp(Y/2) \sqrt{\tau^2 - 4Bk}}{\sinh(Y \sqrt{\tau^2 - 4Bk} / 2\tau)} \\
& + 2 \left(S_b + \tau \ln \frac{\theta_c}{\theta_b} \right) \theta_c \left\{ \div \left\{ -\tau - \frac{(2E - 1) \sqrt{\tau^2 - 4Bk}}{\tanh(Y \sqrt{\tau^2 - 4Bk} / 2\tau)} + \right. \right. \\
& \frac{E - 1 + E \exp(Y) \sqrt{\tau^2 - 4Bk}}{\exp(Y/2) \sinh(Y \sqrt{\tau^2 - 4Bk} / 2\tau)} + \\
& \left. \left. \left(S_b + \tau \left[\theta_h \left(\ln \frac{\theta_h}{\theta_a} - 1 \right) - \theta_c \left(\ln \frac{\theta_c}{\theta_a} - 1 \right) \right] \right) \right\} \right\}
\end{aligned}$$

for $\tau^2 > 4Bk$ and $|B| > 0$.

Application of Equations (3-24), (3-30), and (3-12) yields

$$\text{C.O.P.} = \left[(E - 1)(Y/2 + 1) - E \exp(Y/2) + \left(S_b + \tau \ln \frac{\theta_c}{\theta_b} \right) \frac{Y \theta_c}{\tau} \right] \div \quad (3-33)$$

$$\left[\frac{2YBk}{\tau^2} - 1 - \frac{2}{Y}(2E - 1) + \frac{2[E - 1 + E \exp(Y)]}{Y \exp(Y/2)} + \right.$$

$$\left. \frac{Y}{\tau} \left[S_b + \tau \left(\theta_h \left(\ln \frac{\theta_h}{\theta_a} - 1 \right) - \theta_c \left(\ln \frac{\theta_c}{\theta_a} - 1 \right) \right) \right] \right]$$

for $\tau^2 = 4Bk$ and $B > 0$.

By combining Equations (3-25), (3-30), and (3-13)

$$\text{C.O.P.} = \left[\tau(E - 1) + \frac{(E - 1)\sqrt{4Bk - \tau^2}}{\tan(Y\sqrt{4Bk - \tau^2}/2\tau)} - \frac{E \exp(Y/2)\sqrt{4Bk - \tau^2}}{\sin(Y\sqrt{4Bk - \tau^2}/2\tau)} \right] \quad (3-34)$$

$$+ 2(S_b + \tau \ln \frac{\theta_c}{\theta_b}) \theta_c \Big] \div \left[-\tau - \frac{(2E - 1)\sqrt{4Bk - \tau^2}}{\tan(Y\sqrt{4Bk - \tau^2}/2\tau)} + \right.$$

$$\left. \frac{E - 1 + E \exp(Y)\sqrt{4Bk - \tau^2}}{\exp(Y/2) \sin(Y\sqrt{4Bk - \tau^2}/2\tau)} + 2 \left(S_b + \tau \left[\theta_h \left(\ln \frac{\theta_h}{\theta_a} - 1 \right) - \theta_c \left(\ln \frac{\theta_c}{\theta_a} - 1 \right) \right] \right) \right]$$

when $4Bk > \tau^2$ and $B > 0$.

Application of Equations (3-26), (3-30), and (3-15) produces

$$\text{C.O.P.} = \left[\exp(Y) \left(\frac{\frac{Yk \rho_a}{\tau^2} + (T_h - T_c)}{1 - \exp(Y)} \right) + \frac{k \rho_a}{\tau^2} + \right. \quad (3-35)$$

$$\left. (S_b + \tau \ln \frac{\theta_c}{\theta_b}) \frac{(T_h - T_c)\theta_c}{\tau} \right]$$

$$\div \left[\frac{Yk \rho_a}{\tau^2} + \frac{(T_h - T_c)}{\tau} \left(S_b + \tau \left[\theta_h \left(\ln \frac{\theta_h}{\theta_a} - 1 \right) - \theta_c \left(\ln \frac{\theta_c}{\theta_a} - 1 \right) \right] \right) \right]$$

when $B = 0$.

If $\tau = 0$ and $B > 0$, then Equations (3-27), (3-30), and (3-17) can be combined to yield:

$$\text{C.O.P.} = \left[Bk \left(\frac{(E - 1) \cos(IL\sqrt{Bk}/kA) - E}{\sin(IL\sqrt{Bk}/kA)} \right) + S_b \theta_c \right] \div \left[\sqrt{Bk} \frac{(2E - 1) [1 - \cos(IL\sqrt{Bk}/ka)]}{\sin(IL\sqrt{Bk}/kA)} + S_b \right] \quad (3-36)$$

When $\tau = 0$ and $B = 0$, Equations (3-28) and (3-29) give

$$\text{C.O.P.} = \frac{\frac{-I^2 \rho_a L}{2A} - \frac{kA(T_h - T_c)}{L} + S_b I T_c}{\frac{I^2 \rho_a L}{A} + S_b I(T_h - T_c)} \quad (3-37)$$

No-Load Temperature Difference

Analytical solutions for the no-load temperature difference cannot be readily found using previous assumptions. In order to obtain the no-load temperature, it would be necessary to change the boundary conditions so that $T = T_h$ at $x = 0$ and $Q_c = 0$ at $x = L$, while T_c is allowed to vary. This, however, violates the assumption that ρ_a is a constant expressed by $\rho_a = (\rho_c + \rho_h)/2$. If T_c is allowed to vary, then ρ_a will vary and, hence, can no longer be considered as a constant. The same problem exists with $S_b = (S_c + S_h)/2$. Various values of τ and B cannot be compared, and still have the average Seebeck coefficient, S_b , and average resistivity, ρ_a , remain constant. However, Norwood's paper (14) deals with the effects of the Thomson coefficient and variable resistivity on the no-load temperature difference. The results of his paper will be presented in place of analytical results for the no-load temperature

difference.

Analytical equations for the heat removed and the coefficient of performance for the element have been presented. These equations, which were developed from the basic equation for temperature distribution within a thermoelement, are the six possible solutions for Q_c and C.O.P. under the imposed conditions of operation. The substitution of numerical values into the equations in order to determine the numerical effect of τ and variable ρ on performance remains to be completed in the following chapters.

CHAPTER IV

RESULTS

Numerical Solutions for the Performance Equations

The temperature distribution, the rate of heat removal, and the coefficient of performance of an insulated thermoelement operated as a heat pump can be determined by applying the equations presented in Chapter III. The complexity of these equations prevents predicting the influence of the Thomson coefficient and variable resistivity on thermoelement performance directly from the equations. In order to analyze the influence of τ and variable ρ on heat pump performance, a numerical example has been completed. The following values for the physical dimensions and properties of a thermoelement were used in the example:

$L = 1.0 \text{ cm}$	$\rho_a = 0.001 \text{ ohm-cm}$
$k = 0.02 \text{ watt/cm-}^\circ\text{K}$	$T_a = T_b = 275^\circ\text{K}$
$A = 0.370 \text{ cm}^2$	$T_c = 250^\circ\text{K}$
$S_b = 212 \times 10^{-6} \text{ volts/}^\circ\text{K}$	$T_h = 300^\circ\text{K}$

The Thomson coefficient was analyzed for $\tau = 0, \pm 100, \pm 150, \text{ and } \pm 200 \times 10^{-6} \text{ volts/}^\circ\text{K}$, while B was assumed to have values of 0, 1, 2, 4, and $6 \times 10^{-6} \text{ ohm-cm/}^\circ\text{K}$. The values for the constants and the range of values for τ and B were partially selected because they conform to the properties of thermoelectric materials presently available. Negative values of B were not considered because thermoelectric heat pump materials presently in use have resistivities that increase with temper-

ature. In order to correlate Norwood's results (14) with the results of this thesis, values for the constants listed above closely approximate the values used in his paper. A table of the properties of various thermoelectric materials is presented in Appendix B for reference.

The Burroughs 220 Computer was used to substitute the constants and the various combinations of τ and B into the appropriate equations for Q_c and C.O.P. in order to obtain numerical solutions. For each combination of τ and B , the computer determined the two currents which would produce the theoretical maximum heat removal, Q_{cmax} , and the maximum coefficient of performance, C.O.P._{max}. The computer then calculated a C.O.P. using the current for which heat removal is maximum. This C.O.P. corresponding to the point of Q_{cmax} is designated C.O.P._i. Similarly, the computer calculated a Q_c using the current for which coefficient of performance is maximum. This Q_c corresponding to the point of C.O.P._{max} is designated Q_{cj} . A more detailed description of the computer program is presented in Appendix C. Figures 4 and 5 were plotted from the compiled results.

For simplicity in interpreting the two graphs, the values of heat removal and coefficient of performance were normalized by dividing them by a reference value, Q_{cref} and C.O.P._{ref}, respectively. Q_{cref} was taken as 0.150 watts and C.O.P._{ref} was taken as 0.158. These were the values for Q_{cmax} and C.O.P._{max}, that were obtained when τ was zero and B was zero. These values were used because they represent the values that are obtained for the thermoelement if a constant parameter approach is used. In Figure 4 the normalized values of Q_{cj} and Q_{cmax} are plotted as a function of the absolute Thomson coefficient, $|\tau|$. Figure 5 shows

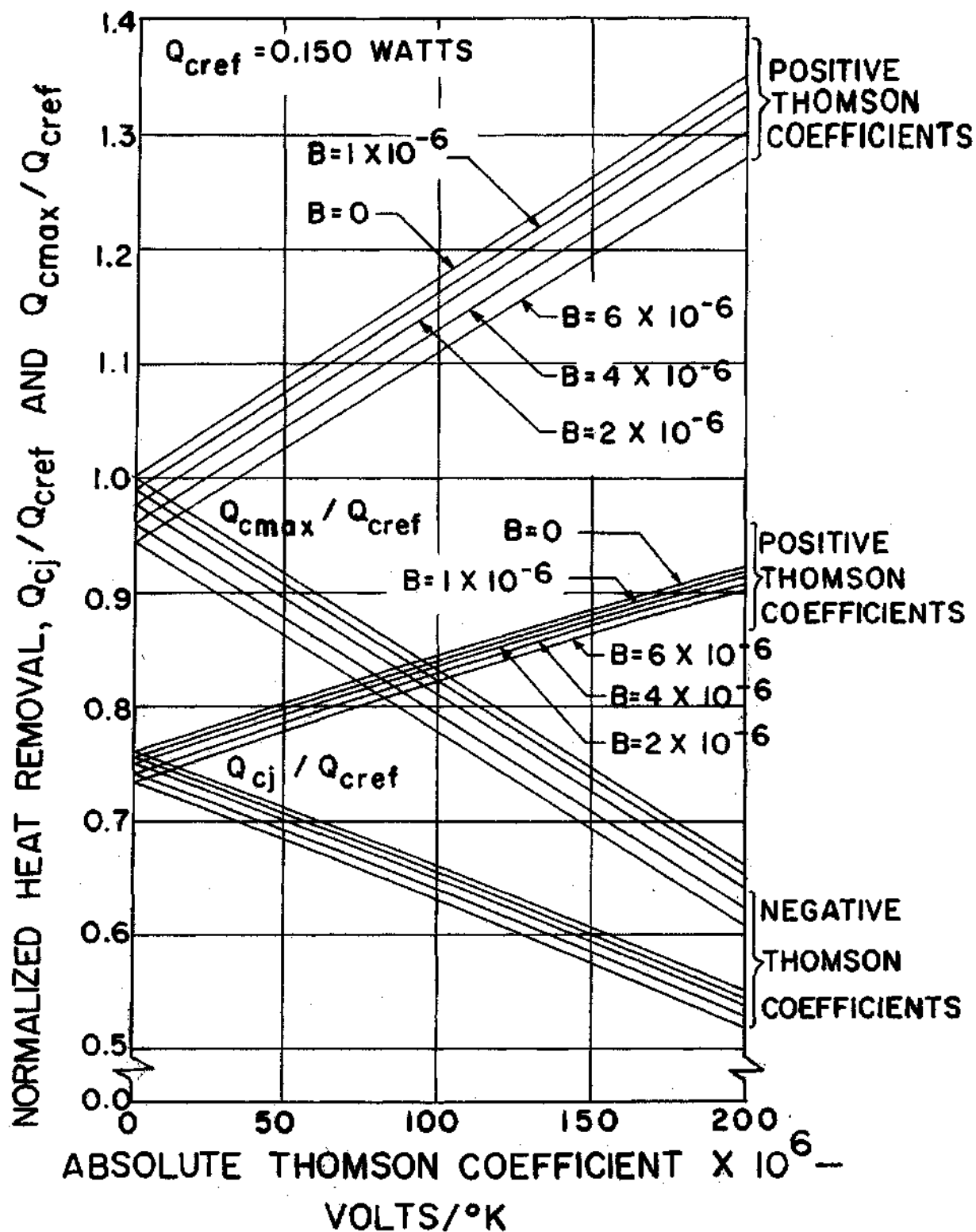


Figure 4. Effect of Thomson Coefficient on the Rate of Heat Removal.

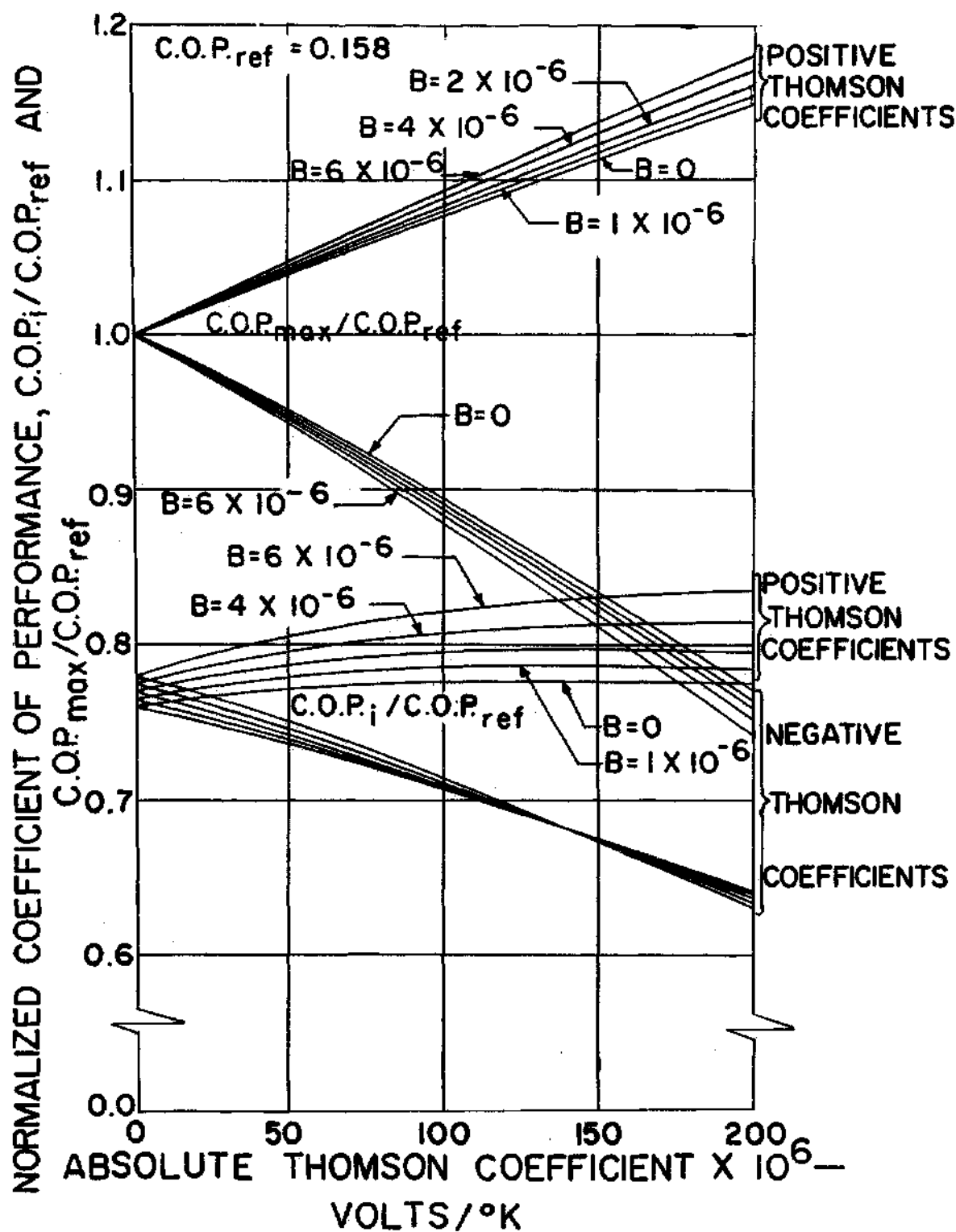


Figure 5. Effect of Thomson Coefficient on the Coefficient of Performance.

the normalized values of $C.O.P._i$ and $C.O.P._{max}$ plotted versus absolute Thomson coefficient. Also plotted on the two graphs are curves for each of the assumed values of the slope B .

Generally, the graphs indicate that the Thomson coefficient has a substantial effect on element performance. The effect of variable resistivity on performance--although not as large as the effect of the Thomson coefficient--is significant under certain operating conditions.

The Effect of Thomson Coefficient on Performance

From Figure 4 it can be seen that a higher value of heat removal is obtained when a positive value for the Thomson coefficient is used rather than a negative value. It is also evident from the graph that as τ increases the heat removal also increases. Since a positive Thomson coefficient, as previously defined, tends to remove heat along the length of the thermoelement, it improves heat removal from the cold end. The improvement in maximum heat removal of an element with a Thomson coefficient of 200×10^{-6} volts/ $^{\circ}$ K over an element with zero Thomson coefficient is about 35 per cent. Negative values of τ have the opposite effect. When τ was -200×10^{-6} volts/ $^{\circ}$ K rather than zero, a decrease in maximum heat removal of about 34 per cent occurred. Therefore, any increase in the Thomson coefficient would be expected to cause an increase in Q_c .

Figure 5 indicated that τ has a similar influence on the coefficient of performance; i.e., $C.O.P.$ generally increases as τ increases. The increase in the maximum $C.O.P.$ of a thermoelement with a Thomson coefficient of 200×10^{-6} volts/ $^{\circ}$ K over a thermoelement with $\tau = 0$ is

approximately 18 per cent. The decrease in maximum C.O.P. if $\tau = -200 \times 10^{-6}$ volts/ $^{\circ}$ K rather than zero is about 26 per cent. Equation (3-29), which defines C.O.P., best illustrates why an increase in C.O.P. would be expected to occur as τ increases. When operating at C.O.P._{max}, changes in τ generally produce only small changes in the denominator (the power input to the element) as compared to the numerator (the heat removal for the element). When the current is adjusted for maximum C.O.P., the C.O.P. tends to vary as the rate of heat removal varies; therefore, C.O.P. increases with increasing τ . For C.O.P._i (Figure 5), this trend is reversed at higher values of τ because of the increased influence of the power input term (the denominator) on the coefficient of performance. As τ is increased, the input current required to maintain maximum heat removal in the element increases also. Although this increase in current produces additional heat removal in the thermoelement, it also produces a greater power input to the element. As τ becomes increasingly large, a point is reached where the power input begins to increase much more rapidly than the heat removed. At this point the coefficient of performance begins to decrease despite increasingly positive Thomson coefficients. As can be seen in Figure 5, C.O.P._i decreases slightly at the higher values of Thomson coefficient.

Use of Results from Norwood

Norwood's results (14) concerning the effect of τ and ρ on the maximum temperature difference, ΔT_{max} , are reproduced in Figure 6. It should be pointed out that these curves were plotted by Norwood using a computer solution to solve the basic differential equation for the

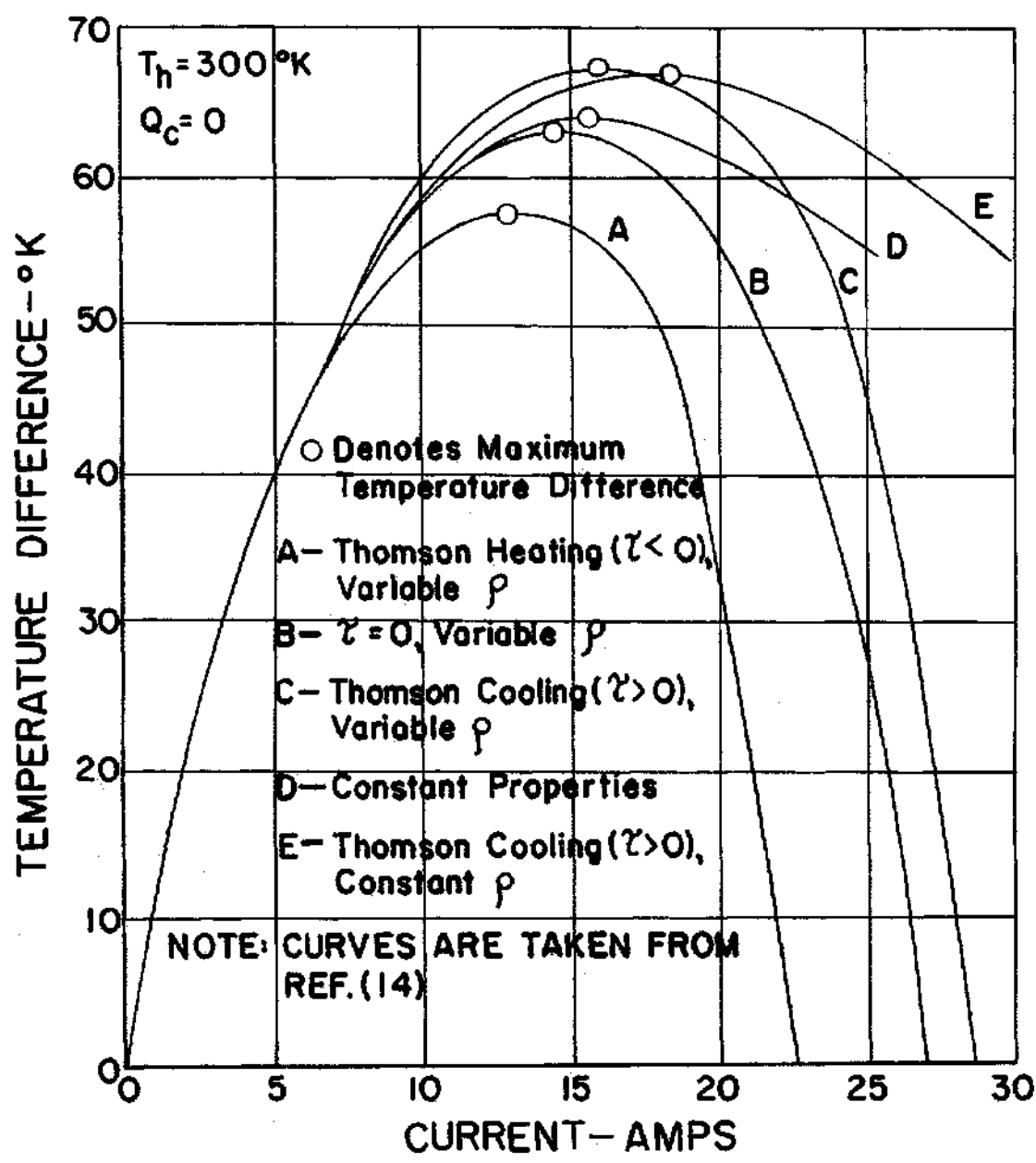


Figure 6. No-Load Temperature Difference as a Function of Current.

temperature distribution within a thermoelement. Norwood assumed that τ varied with temperature; whereas, this thesis assumes that τ is constant. Norwood's results, therefore, are used only to indicate generally the effect that positive and negative Thomson coefficients will have on the maximum temperature difference attainable. As shown by Curve C, a positive Thomson coefficient increases the maximum temperature difference slightly (about 4°K) above that of an element with zero Thomson coefficient (Curve B). A negative value of τ (Curve A) decreases the maximum temperature difference by approximately 5°K .

The Effect of Variable Resistivity on Performance

Figures 4 and 5 indicate how linearly varying resistivity affects the heat removal and coefficient of performance. Increasing B from 0 to $6 \times 10^{-6} \text{ ohm-cm}/^{\circ}\text{K}$, for example, decreases Q_{cmax} by 5 per cent when τ is maintained at $200 \times 10^{-6} \text{ volts}/^{\circ}\text{K}$ (Figure 4). For all cases covered in this thesis, the heat removal was highest when the resistance did not vary with temperature ($B = 0$). When $B = 0$, the Joule heat, $\frac{I^2 \rho_a L}{A}$, is constant for all positions along the thermoelement; so that due to the linear nature of the governing equations half the Joule heat would be conducted to the hot junction, and half to the cold junction. When $B > 0$, the Joule heat is not evenly distributed. Instead, more Joule heat will be concentrated at the points of higher temperature where $T > T_a$, since the resistivity will be greater at these points according to Equation (2-3). Likewise, resistivity will be less than ρ_a at points where $T < T_a$, and Joule heat must be less also.

How heat removal is affected by a change in B can best be eval-

uated by first plotting curves of the thermoelement temperature distribution (Figure 7) for $B = 0$ and $B = 6 \times 10^{-6}$ ohm-cm/ $^{\circ}$ K. The Thomson coefficient is assumed to be zero, and all other properties are constant. The current is taken as 20 amps. This value is approximately the current required for maximum heat removal. The two upper curves are plotted by substitution of the values for the thermoelement properties into Equations (3-17) and (3-19). These two curves are shown as the sum of two separate effects. The straight line is the temperature distribution created by heat conduction through an element with a constant k of 0.02 watt/cm- $^{\circ}$ K and a temperature difference of 50 $^{\circ}$ K. Since the Thomson coefficient is zero, the only other contributor to the temperature distribution is the Joule heat. Siegl and Chaddock (18) have, in fact, shown that the temperature distribution in a thermoelectric element is just a summation of the contributions due to thermal conductance and Joule heat if the Thomson coefficient is zero. The curves for the Joule effect were obtained by plotting the difference between the overall temperature distribution curves and the curve for thermal conductance.

The temperature distribution caused by Joule heat is of primary interest. The curve for $B = 0$ is seen to be symmetrical, which further illustrates that Joule heat flows equally to the hot and cold junctions when resistivity is constant. It is also evident from the curves that the heat flux into the cold junction,

$$\left. \frac{kA(T_h - T_c)}{L} \frac{d\theta}{du} \right|_{u=1}$$

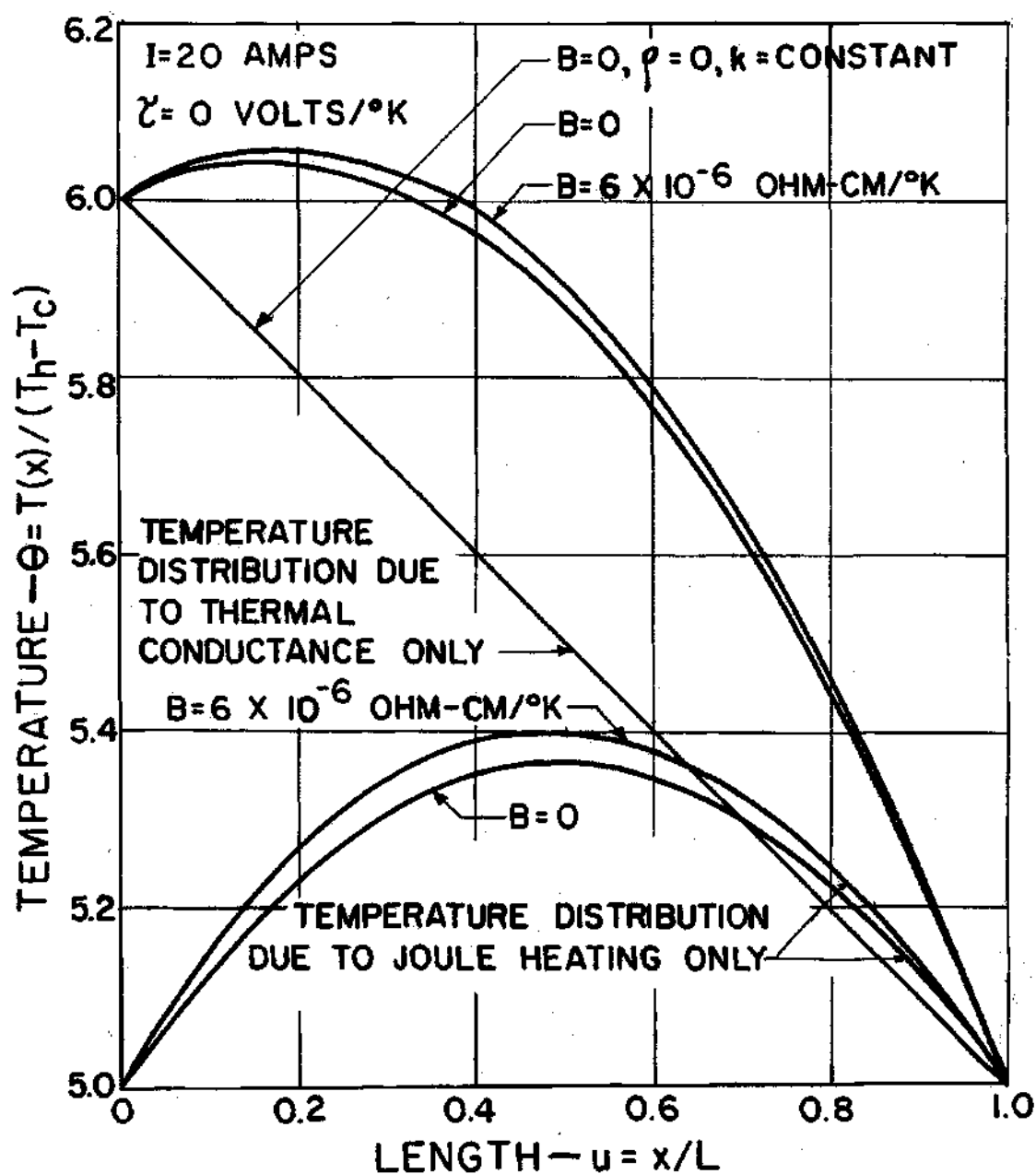


Figure 7. Temperature Distribution in a Thermoclement Without Thomson Effect.

is slightly greater when $B = 6 \times 10^{-6}$ ohm-cm/ $^{\circ}$ K, because the slope, $\left. \frac{d\theta}{du} \right|_{u=1}$, is greater. As stated in Equation (3-20), the heat removal at the cold junction is dependent upon two terms; the heat flux at the cold junction and the Peltier effect. Since the Peltier effect will be constant if the current remains constant, then any difference in heat removal which occurs when B is varied must be a result of changes in heat flux. Higher values of B produce greater heat fluxes, which reduce the rate of heat removal.

The increase in heat flux at the cold junction when B is increased can be attributed to the increase in the element resistivity. The resistivity, as defined previously, is:

$$\rho = \rho_a + B(T - T_a) \quad (2-3)$$

This relationship is used to compare materials having the same average resistivity between the hot and cold junction temperatures. However, it should be noted that although materials with different resistivity slopes will have the same average resistivity, the thermoelements constructed of these materials may not have the same average resistivity over their length. The reason is the non-linear temperature distribution along the length of the thermoelement. As shown in Figure 7, the temperature distribution is normally not linear unless only thermal conductance occurs in the element. The distribution that normally exists produces a mean value of temperature* within the element that is higher

* The mean temperature is defined as: $\theta_{\text{mean}} = \int_0^1 \theta(u) du$.

than the average of the hot and cold junction temperatures, $(\theta_c + \theta_h)/2$. In fact, Figure 7 indicates that over 75 per cent of the length of the element the temperature is above the average temperature, $\theta_a = T_a / (T_h - T_c) = 5.5$. Then, for all values of B , the element resistivity, ρ , will be higher than the average resistivity, ρ_a , over approximately 75 per cent of the element length. As B increases, the resistivity decreases over the 25 per cent of the thermoelement near the cold junction where $T > T_a$ and increases over the other 75 per cent of the length in accord with Equation (2-3). The effect of increasing B is an increase in the overall resistance for the element, and, hence, a rise in Joule heat occurs. The increased Joule heat causes the heat removal, Q_c , to be diminished.

The influence of the resistivity on the coefficient of performance was somewhat different from its effect on heat removal. In fact, due to the complexity of the equations, its influence is difficult to evaluate. Figure 5 indicated that for positive Thomson coefficients, a greater value of $C.O.P._{max}$ was obtained when B increased. A maximum of 8 per cent improvement in C.O.P. occurs when B increases from zero to 6×10^{-6} ohm-cm/ $^{\circ}$ K. For negative Thomson coefficients, best performance was achieved when B approached zero. When $\tau = 0$, the maximum C.O.P. was the same value for all values of B . It would appear, therefore, that $C.O.P._{max}$ is always independent of B when $\tau = 0$. Equations (3-36) was differentiated with respect to the current and set equal to zero in order to maximize the C.O.P. when $\tau = 0$. The resulting equation could not be evaluated or simplified in such a manner that $C.O.P._{max}$ could be shown to be independent of B when $\tau = 0$. A similar point where all curves intersected also occurred for $C.O.P._i$ at $\tau = -135 \times 10^{-6}$ volts/ $^{\circ}$ K.

Norwood's results shown in Figure 6 indicate how resistivity affects the maximum temperature difference. When $\tau = 0$, ΔT_{\max} is improved very slightly for a variable resistivity with $B > 0$ (Curve C) rather than constant resistivity (Curve E). From these two curves a change in resistivity with temperature appears to have almost negligible effect on ΔT_{\max} .

In summary the computer results have shown that the relative influence of τ and variable resistivity on Q_c , C.O.P., and ΔT_{\max} , varies sharply with the operating conditions for the thermoelement; i.e., with operation at maximum heat removal or at maximum coefficient of performance.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Equations were presented for predicting the temperature distribution, heat removal, and coefficient of performance for a heat pump element with a constant Thomson coefficient and variable resistivity. The numerical results, which were applications of these equations to specific cases, have delineated the effect of Thomson coefficient and variable resistivity on element performance. These results showed among other things that a constant parameter approach can yield values for heat removal and coefficient of performance that are in considerable error. As much as 35 per cent difference in the heat removal and 18 per cent difference in the coefficient of performance occurred when the Thomson effect was included in the theoretical analysis. In a similar manner, Norwood demonstrated that a variation in the maximum temperature difference of several degrees Kelvin was experienced when τ took on values other than zero.

The use of a linearly varying resistivity in the theoretical equations as opposed to a constant value for ρ can also alter thermoelement performance. As high as 8 per cent change in the coefficient of performance was noted between a material with constant resistivity and a material whose resistivity was a linear function of temperature. Therefore, any theoretical analysis of heat pump performance should include Thomson coefficient and variable resistivity.

The analysis also revealed that heat pumps constructed with materials having large positive values of Thomson coefficient will, in general, produce a higher rate of heat removal, a better coefficient of performance, or a greater temperature difference than thermoelements with low or negative Thomson coefficients. If the thermoelement is to be operated at the point of maximum Q_c , C.O.P., or ΔT , it would be advantageous to select a thermoelectric material that has a large, positive Thomson coefficient. Provided all other properties are the same, the available material with the highest value of τ should be chosen.

Heat pump performance can also be improved by selecting the thermoelectric material having certain resistivity characteristics. The results indicated that a constant rather than a variable resistivity should be chosen for better heat removal. For positive values of τ , better coefficients of performance can be attained by using a material with a variable resistivity rather than constant resistivity. The effect of variable resistivity on the maximum temperature difference is negligible.

It is evident that the Thomson coefficient and variable resistivity are both important properties that should be considered when selecting thermoelectric materials for heat pumps. The extent to which they may affect element performance is dependent upon the operating conditions for the heat pump.

The closed form solutions presented in Chapter III permit the substitution of any desired values of I and the constants k , L , A , T_h , T_c , ρ_a , and S_b to obtain Q_c and C.O.P. Other operating conditions can, therefore, be evaluated using the same techniques employed in this thesis. For this reason, these equations should be useful for assisting

in the determination of the correct thermoelectric material for a particular heat pump application.

It is recommended that further studies be carried out to more accurately establish the effect of constant Thomson coefficient and variable resistivity on the maximum no-load temperature difference. Norwood's paper indicated the general effect of ρ and variable τ on ΔT , but did not analyze this effect for various values of τ and B . To do this, it will be necessary to make some different assumptions than were made for this thesis. One possible approach might be to assume a constant temperature at the hot junction, T_h . Let $Q_c = 0$ at $x = L$, while T_c is allowed to vary. The expression for resistivity and Seebeck coefficient could be written as:

$$\rho = \rho_h + B (T - T_h) \quad (5-1)$$

and

$$S = S_h + \tau \ln T/T_h \quad (5-2)$$

in order to develop closed form equations for the maximum temperature difference. In addition, this would permit materials to be compared, which have the same value of resistivity and Seebeck coefficient at the hot junction, but which can have different values of Thomson coefficient and linearly varying resistivity.

APPENDIX A

DERIVATION OF THE ONE-DIMENSIONAL DIFFERENTIAL EQUATION
FOR THE TEMPERATURE DISTRIBUTION IN AN INSULATED THERMOELEMENT

Consider a thermoelement of differential length dx as shown in Figure 8. It is assumed that the electrical current I is constant; the cross-sectional area, $A(x)$, is an arbitrary function of x ; the element is insulated along its entire length; the temperature is uniform across any section perpendicular to the x -axis; and that steady state conditions prevail. Under these conditions, the rate of energy flow into the element must be equal to the rate of energy flow out of the element so that

$$\left(\frac{dU}{dt}\right)_{in} - \left(\frac{dU}{dt}\right)_{out} = 0 \quad (A-1)$$

The rate at which energy flows into the element due to heat conduction at position x is

$$+ kA \frac{dT}{dx} \quad (A-2)$$

The rate at which electrical energy enters the element at position x is

$$+ IV \quad (A-3)$$

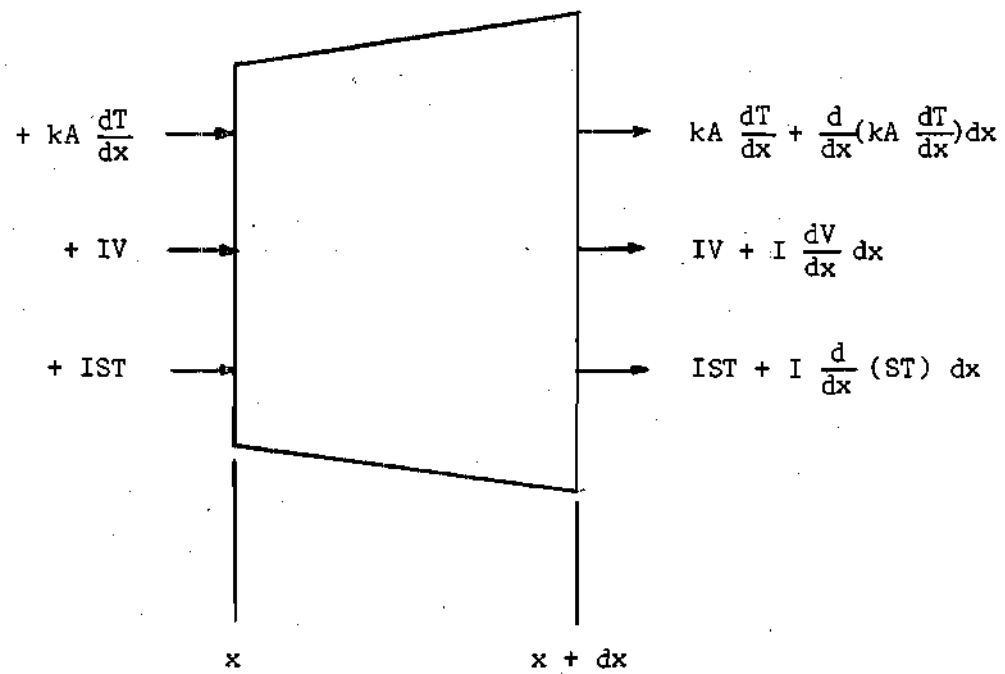


Figure 8. Differential Section of a Thermoelement

The rate at which Peltier heat is liberated at position x is

$$+ IST \quad (A-4)$$

The rate at which energy leaves the element at position $x + dx$ by conduction is

$$+ kA \frac{dT}{dx} + \frac{d}{dx} (kA \frac{dT}{dx}) dx \quad (A-5)$$

The rate at which electrical energy leaves the element at position $x + dx$ is

$$+ IV + I \frac{dV}{dx} dx \quad (A-6)$$

The rate at which Peltier heat is liberated at position $x + dx$ is

$$+ IST + I \frac{d}{dx} (ST) dx \quad (A-7)$$

Substitution of Equations (A-2) through (A-7) into Equation (A-1) gives

$$\frac{d}{dx} (kA \frac{dT}{dx}) + I \frac{dV}{dx} + IT \frac{dS}{dx} + IS \frac{dT}{dx} = 0 \quad (A-8)$$

From irreversible thermodynamics (12) it can be shown that in a non-isothermal rod through which a current passes

$$\frac{dV}{dx} = + I \frac{dR}{dx} - S \frac{dT}{dx} \quad (\text{A-9})$$

where

$$R = \int_0^x \frac{\rho(T) dx}{A(x)} \quad (\text{A-10})$$

or

$$dV = \frac{I\rho}{A(x)} - S \frac{dT}{dx} \quad (\text{A-11})$$

Substitution of Equation (A-11) into Equation (A-8) gives

$$\frac{d}{dx} (kA \frac{dT}{dx}) + IT \frac{dS}{dx} + \frac{I^2 \rho}{A} = 0 \quad (\text{A-12})$$

However,

$$\frac{dS}{dx} = \frac{dS}{dT} \cdot \frac{dT}{dx} \quad (\text{A-13})$$

so that Equation (A-12) becomes

$$\frac{d}{dx} (kA \frac{dT}{dx}) + IT \frac{dS}{dT} \cdot \frac{dT}{dx} + \frac{I^2 \rho}{A} = 0 \quad (\text{A-14})$$

The Thomson coefficient, τ , is defined

$$\tau = T \frac{dS}{dT} \quad (\text{A-15})$$

so that Equation (A-14) may be written

$$\frac{d}{dx} \left(kA \frac{dT}{dx} \right) + I\tau \frac{dT}{dx} + \frac{I^2 \rho}{A} = 0 \quad (\text{A-16})$$

where A is an arbitrary function of x ; k , ρ , and τ are functions of the temperature. If the current is in the opposite direction, which occurs for a heat pump, then

$$\frac{d}{dx} \left(kA \frac{dT}{dx} \right) - I\tau \frac{dT}{dx} + \frac{I^2 \rho}{A} = 0 \quad (\text{A-17})$$

APPENDIX B

Table 1. Properties of Typical Thermoelectric Heat Pump Materials

Alloy	Type	Temperature °K	$\rho \times 10^4$ ohm-cm	$B \times 10^6$ ohm-cm °K	$S \times 10^6$ Volts °K	$\tau \times 10^6$ Volts °K *	$\frac{k}{\text{cm-°K}}$ Watts	Ref.
Bi_2Te_3	N	230		3.55	-160.0	-124.0	0.0220	14
		260		3.55	-174.0		0.0199	
		280		3.55	-182.0		0.0191	
		300	8.0	3.55	-190.0		0.0187	
Bi_2Te_3	P	230		5.72	166.7	168.5	0.0180	14
		260		5.72	185.6		0.0163	
		280		5.72	196.0		0.0156	
		300	11.4	5.72	205.0	115.0	0.0151	
$\text{Bi}_{2.0}\text{Te}_{1.8}\text{Se}_{1.2}$	N	225-50		0.0		- 14.25		5
		250-75		0.0		- 21.0		
		275-300		0.0		- 34.5		
		225		0.0	-161.5			
		250		0.0	-163.0			
		275		0.0	-165.0			
		300	139.0	0.0	-168.0		0.008	
$\text{Bi}_{2.0}\text{Te}_{1.9}\text{Se}_{2.1}$	N	225-50		6.4		- 47.5		5
		250-75		6.4		- 31.5		
		275-300		4.8		- 57.5		
		225			- 82.0			
		250			- 87.0			
		275			- 90.0			
		300	24.4		- 95.0		0.010	
$\text{Bi}_{9.5}\text{Sb}_5$	N	225-50		0.68		29.5		19
		250-75		0.00		32.6		
		275-300		0.72		36.8		
		225			-115.6		0.0475	
		250			-112.5		0.0448	
		275			-109.4		0.0476	
		300	1.5		-106.2		0.0438	

* Values of τ were calculated using the relation: $\tau = T \frac{dS}{dT}$.

APPENDIX C

SAMPLE COMPUTER PROGRAM

Normally, the best way to obtain the maximum heat removal and maximum coefficient of performance would be to differentiate the equations for Q_c and C.O.P. with respect to current, set the resulting expressions equal to zero, and solve for the Current, I . The current obtained would be that current required to produce Q_{cmax} or C.O.P._{max}. However, the equations presented in Chapter III are, as a whole, too difficult to handle in this manner. Therefore, a different technique was employed. The two equations for Q_c and C.O.P. when τ and B are zero (Equations (3-28) and (3-37)) were differentiated to obtain expressions for the current required for maximum heat removal and coefficient of performance. Taking Equation (3-28),

$$Q_c = \frac{-I^2 \rho_a L}{2A} - \frac{kA(T_h - T_c)}{L} + S_b I T_c \quad (3-28)$$

differentiating it with respect to I , and setting it equal to zero, we obtain

$$\frac{dQ_c}{dI} = 0 = \frac{-I \rho_a L}{A} + S_b T_c \quad (B-1)$$

or

$$I = \frac{S_b A T_c}{\rho_a L} \quad (B-2)$$

Similarly,

$$\text{C.O.P.} = \frac{\frac{-I^2 \rho_a L}{2A} - \frac{kA(T_h - T_c)}{L} + S_b I T_c}{\frac{I^2 \rho_a L}{A} + S_b I (T_h - T_c)} \quad (3-37)$$

Differentiating Equation (3-37) with respect to I and setting it equal to zero gives:

$$\frac{d(\text{C.O.P.})}{dI} = 0 = \frac{\rho_a L S_b}{2A} (T_c + T_h) I^2 - \quad (B-3)$$

$$2 \rho_a k (T_h - T_c) I - \frac{S_b k A}{L} (T_h - T_c)^2$$

or

$$I = \frac{S_b (T_h - T_c)}{\frac{\rho_a L}{A} \left(-1 + \sqrt{1 + \frac{S_b^2}{2 \rho_a k} (T_c + T_h)} \right)}$$

Equation (B-4) is the same as that given by Ioffe (10), Equations (B-2) and (B-4) allow the current at maximum Q_c and C.O.P. to be calculated when $\tau = 0$ and $B = 0$. These two currents serve as a means of locating approximately what the values of current for $Q_{c\max}$ and C.O.P._{\max} for other τ and B should be. With this knowledge of current, a range of values for I can then be substituted into the equations for Q_c and C.O.P. The current was substituted at intervals of about 0.10 amps to first establish the approximate values of current for $Q_{c\max}$ and C.O.P._{\max} .

Once the approximate currents are known, a smaller interval of current of 0.01 amps is used to establish the values of maximum heat removal and coefficient of performance to the desired accuracy. The technique is demonstrated by a portion of the computer program that has been retyped below.

First, I was calculated for Q_{cmax} and $\text{C.O.P.}_{\text{max}}$ when τ and B are zero.

$$I = \frac{S_b A T_c}{\rho_a L} = \frac{212 \times 10^{-6} \times 0.37 \times 250}{0.001 \times 1.0} = 19.61 \text{ amps for } Q_{\text{cmax}}$$

$$I = \frac{S_b (T_h - T_c)}{\frac{\rho_a L}{A} \left(-1 + \sqrt{1 + \frac{S_b^2 (T_c + T_h)}{2 \rho_a k}} \right)} =$$

$$\frac{212 \times 10^{-6} \times 50}{\frac{0.001 \times 1.0}{0.370} \left(-1 + \sqrt{1 + \frac{(212 \times 10^{-6})^2 (250 + 300)}{0.001 \times 0.02 \times 2}} \right)} =$$

14.53 amps for $\text{C.O.P.}_{\text{max}}$.

These two currents provided the basis for the range of currents to be substituted into the computer program.

Program (For $B > 0$, $\tau = 0$)

BAC-220 STANDARD VERSION

COMMENT WAYNE L. ADAMSON

COMMENT THERMOELECTRIC HEAT PUMP PROGRAM NO. 3, HC=0

```

ARRAY    QB(500), CB(500), I(500)    $

K=0.02 $ L=1.0 $ AR=0.0370 $ TC=250.0 $ TH=300.0 $ PC=0.001 $

SC=0.000212 $ TA=275.0 $

INTEGER  J $

WRITER ($$TITLE)    $

FOR B=0.000006,0.000004,0.000002,0.000001    $

FOR J=(130,1,200)    $

BEGIN    I(J)=0.10(J)    $

        QB(J)=(TH-TC).I(J).SQRT(B.K)/(((PC/B(TH-TC))-0.5).COS(I(J).L.
SQRT(B.K)/(K.AR))-((PC/B(TH-TC))+0.5))/(SIN(((B.K)*0.5).I(J).L/(K.AR))
+ SC.I(J).TC    $

        CB(J)=(QB(J))/((I(J).(TH-TC).SQRT(B.K).(2PC/B(TH-TC))
(1.0-COS(I(J).L.SQRT(B.K)/(K.AR)))/(SIN(I(J).L.SQRT(B.K)/(K.AR)))) +
I(J))(SC.(TH-TC)))    $

WRITE($$ANS,FMT)    END    $

READ($$DATA)    $

INPUT    DATA(NONE)    $

OUTPUT    ANS(I(J),QB(J),CB(J),B)    $

FORMAT    TITLE(B16,*I(J)*,B16,*QB(J)*,B15,*CB(J)*,B19,*B*,W3,W2)    $

FORMAT    FMT(4S20.8,W0)    $

FINISH    $

```

Sample Printout

I(J)	QB(J)	CB(J)	B
13.00	0.09479239	0.15560263	0.00000600
13.10	0.09651168	0.15622495	0.00000600

----	----	----	----
----	----	----	----
13.80	0.10766683	0.15841226	0.00000600
13.90	0.10913362	0.15844748	0.00000600
14.00	0.11056839	0.15842070	0.00000600
14.10	----	----	----
----	----	----	----
18.00	0.14043037	0.12513287	0.00000600
18.10	0.14045272	0.12381616	0.00000600
18.20	0.14043760	0.12248625	0.00000600

etc.

The numbers which are enclosed are approximately the maximum values of C.O.P. and Q_c for $\tau = 0$ and $B = 0.00000600$. Another computer program would be utilized to establish the current to the nearest 0.01 amps rather than 0.10 amps. The only change in the second program over the first one would be the change in the range of current I.

In the program the following notations were used:

QB = Heat removal.

CB = Coefficient of performance.

I = Current.

PC = Average resistivity.

SC = Average Seebeck coefficient.

HC = Thomson coefficient.

B = Slope of the resistivity.

TC = Temperature at the cold junction.

TH = Temperature at the hot junction.

TA = Average temperature corresponding to the average Seebeck coefficient and the average resistivity.

AR = Area of the thermoelement.

L = Length of thermoelement.

K = Thermal conductivity of the element.

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